

Molecular and crystal structures of 2-phenyl-2-hydro-6-methyl-1,3-dioxo-6-aza-2-silacyclooctane

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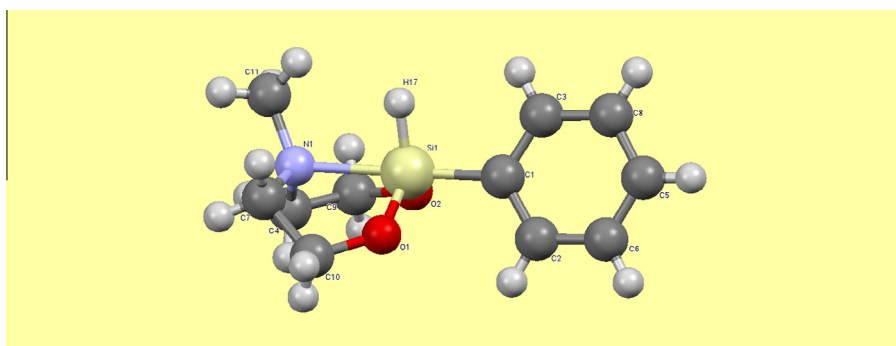
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HIGHLIGHTS

- X-ray structure is determined.
- Structures of various molecular conformations are optimized at B3LYP and MP2 levels of theory.
- Molecular structure in crystalline state is compared with the structure of conformers proposed for liquid state.

GRAPHICAL ABSTRACT



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ABSTRACT

The crystal structure of 2-phenyl-2-hydro-6-methyl-1,3-dioxo-6-aza-2-silacyclooctane [HPhSi(OCH₂CH₂)₂NMe – phenylhydrosiloxane (I)] is determined by single-crystal X-ray diffraction at 100 K. The unit cell consists of four molecules connected only by Van-der-Waals interactions. Each molecule has an eight-membered heterocycle with a phenyl group in the axial position. The Si···N transannular bond has a short (2.206 Å) interatomic distance which exceeds only this distance in oxanes with highly electronegative fluorine substituents at Si. Since there exist experimental data on the occurrence of different conformers of I in the liquid phase, the PES of the molecule was analyzed by DFT B3LYP and MP2 methods with the aug-cc-pVDZ basis set. The energy minimum belongs to the boat–chair conformation with the axial position of the phenyl group. Rotation of the phenyl ring around the SiC bond has a barrier ca. 1 kcal/mol. The conformer with the equatorial position of this group lies 6 kcal/mol higher. Interconversion of this conformers which was observed in experiment proceeds through the chair–chair configuration in which the Si···N transannular bond is absent and coordination at silicon is tetrahedral, rather than trigonal bipyramidal one observed in other conformers.

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Introduction

Siloxanes XYSi(OCH₂CH₂)₂NR (aka quasisilatrane) are analogues of better known silatrane XSi(OCH₂CH₂)₃N. In contrast to

the latter they contain only two SiOCH₂CH₂N heterocycles. As well as tricyclic silatrane, bicyclic siloxanes are highly promising biologically active products [1]. Several molecular structures already have been determined by X-ray diffraction: X = Y = Ph, R = H (II) [2], X = Y = Ph, R = Me (III), X = Y = Ph, R = CMe₃ (IV), X = Y = Me, R = Ph (V), X = Y = Ph, R = Ph (VI) [3], X = Y = F, R = H (VII) [4], X = F, Y = Ph, R = Me (VIII) [5], X = F, Y = Me, R = H (IX) [6]. The

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major part of the determined silocane structures [II,III,VIII,IX] have a boat–boat (BB) configuration of eight-membered heterocycles Si–(OCC)₂–N while structures IV and VII have boat–chair configurations of the skeleton. In all these structures the short Si···N contact (with the exception of IV) is observed which vary within the 1.98–2.30 Å range thus indicating a N → Si donor–acceptor bond.

Two structures are known (V and VI) which possess chair–chair conformations [3] and in which Si–N interatomic distances are substantially longer (3.08–3.19 Å).

The NMR study of Ar₂Si(OCH₂CH₂)₂NR compounds [7] revealed the occurrence in solution of an equilibrium between boat–boat (with Si–N transannular bond) and chair–chair (without transannular bond) conformations. In ocanes with different substituents at Si (X ≠ Y) there exists a possibility of isomers differing by their position in the trigonal bipyramidal configuration at silicon. In the NMR study [8] of HPhSi(OCH₂CH₂)₂NCH₃ (I) it was shown that there exist two isomers and they correspond to the axial and equatorial arrangement of the phenyl group.

However, the presence of only one SiH stretching band in the IR spectrum of HPhSi(OCH₂CH₂)₂NCH₃ [9,10] both in liquid and solids phases allows authors to propose that the boat–chair conformation is predominant in solution and that the content of the structures with axial position of the H atom is low [9]. There are no doubts that the phenyl group in crystalline phenylhydrosilocane (I) occupies the axial position, since in the known structures of ocanes with different substituents at Si, that are FPhSi(OCH₂CH₂)₂NCH₃ (VIII) and FMeSi(OCH₂CH₂)₂NH (IX), more electronegative substituent occupies the axial position. However, no X-ray data on I exist. Our interest in this compound is also explained by the fact that we intend to use this compound as a source of nucleogenic [11] cations PhSi⁺(OCH₂CH₂)₂NMe. In the second part of our study we used quantum chemical methods to bring light on plausible isomers of I and the mechanisms of their interconversion.

Experimental and computational details

The title compound was prepared by the reaction of phenylsilane with methyldiethanolamine [12]. It crystallizes as colorless crystals from hexane solution. The synthesized product was identified by ¹H and ¹³C NMR spectra. Five groups of signals were observed, those are a singlet at 2.43 ppm, double triplets with the average shift of 2.81 ppm, a group of lines at 3.94 ppm, singlet at 5.15 ppm and two group of lines in the 7.2–7.6 ppm range. In the ¹³C NMR spectrum signals corresponding to phenyl ring carbons (143.3, 133.7, 128.8, 128.9 ppm) to methylene groups (68.2, 55.1 ppm) and to the methyl group (41.9 ppm) were observed. These spectra coincide with the NMR spectra earlier reported for 2-phenyl-2-hydro-6-methyl-1,3-dioxo-6-aza-2-silacyclooctane by Kupce et al. [8].

An isometric specimen of C₁₁H₁₇NO₂Si, approximate dimensions 0.16 mm × 0.19 mm × 0.23 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Saxon-CrysAlisPro CCD system equipped with a graphite monochromator and a Mo Kα sealed tube (λ = 0.71073 Å). Data collection temperature was 100 K.

The frames were integrated with the Agilent Technologies CrysAlisPro software package [13]. The integration of the data using a monoclinic unit cell yielded a total of 5723 independent reflections to a maximum θ angle of 37.28°, (completeness = 99.9%, R_{int} = 7.74%) and 3281 were greater than 3σ(F). The final cell dimensions *a* = 9.9205(7) Å, *b* = 9.5937(5) Å, *c* = 12.2489(8) Å, β = 108.860(7)°, *V* = 1103.19(12) Å³, with 2.17° < 2θ < 37.28°. Data were corrected for absorption effects using the multi-scan method and using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.931 and 1.0. The

structure was solved and refined using the SIR2011 Software Package [14], using the space group P21/c, with *Z* = 4 for the formula unit C₁₁H₁₇NO₂Si. The final anisotropic full-matrix least-squares refinement on *F* with 81 variables converged at *R*₁ = 0.042, for the observed data and *wR*₂ = 0.049 for all data. The goodness-of-fit was 0.988. The carbon and nitrogen-bound H atoms were placed in calculated positions and were included in the refinement in the rigid body approximation, with *U*_{iso}(H) set to 1.2*U*_{eq}(C) and C–H 0.97 Å. Positions of atom H₁₇ were localized from difference Fourier maps and refined without any restrictions, with individual isotropic temperature parameters. The largest peak in the final difference electron density synthesis was 0.24 e/Å³ and the largest hole was –0.23 e/Å³ with an RMS deviation of 0.145 e/Å³. On the basis of the final model, the calculated density was 1.345 g/cm³ and *F*(000) = 480 e. (CCDC number is 000100021398).

Geometries of stationary points have been fully optimized and characterized by harmonic vibrational frequency calculations using the B3LYP [15,16] density functional method and the second-order Moller–Plesset perturbation theory (MP2) with the frozen core approximation [17]. The Dunning correlation-consistent sets aug-cc-pVDZ [18] was employed. All the methods and basis sets were used as implemented in the Gaussian09 program [19].

Results and discussion

The structure of 2-phenyl-2-hydro-6-methyl-1,3-dioxo-6-aza-2-silacyclooctane obtained in the X-ray study is depicted in Fig. 1. Coordinates of atoms of 2-phenyl-2-hydro-6-methyl-1,3-dioxo-6-aza-2-silacyclooctane obtained in the X-ray study together with isotropic displacement parameters, bond lengths, and angles are listed in Tables S1–S3 in supplementary materials.

Similar to structures of other silocanes refined earlier [2–6] the coordination geometry of silicon is close to trigonal bipyramidal with a phenyl group in the axial position. The average C1–Si–O angle in this trigonal bipyramid is 97.9(2)°, while the C1–Si–H17 angle is 95(2)°. Note, that in other ocanes containing one phenyl group, that is FPhSi(OCH₂CH₂)₂NCH₃ (VIII), phenyl group is in equatorial position. Obviously, more electronegative substituent occupies an axial position.

Silicon lies practically on the plane formed by the equatorial atoms O1, O2, and H17 (the deviation from this plane towards the phenyl ring is only 0.189 Å). The phenyl ring plane is slightly twisted from the N1–Si1–H17 plane [the dihedral angle H17–Si1–C1–C3 is –21.5(2)°].

The intramolecular SiN bond divides the Si(OCH₂CH₂)₂N eight-membered heterocycle to two five-membered heterocycles SiOCCN. As in silatranes these heterocycles are nonplanar.

In both five-membered heterocycles carbon atoms located in the α-position to nitrogen are deflected from the SiOC_βN plane. Bond lengths in the Si–(OCC)₂–N heterocycle do not differ substantially from corresponding distances in other silatranes and silocanes (Table S2 in Supplementary materials).

The substitution of electronegative oxygen atom in 1-phenylsilatrane for more positive hydrogen leads to the shortening of the Si···N transannular bond from 2.312 Å in silatrane [20] to 2.206 Å in the studied ocanes. However, the substitution of H by another phenyl group in II leads to a substantial increase of the Si···N distance (2.260 Å) [3]. Note, that the Si···N distance depends not only on substituents at Si but also at N. Thus, this distance in Ph₂Si(OCH₂CH₂)₂NR compounds grows from 2.30 Å for R = H to 3.16 Å for R = CMe₃. Nevertheless, the shortest transannular bond (1.981 Å) is in silocane with two fluorine substituents [5]. However in FPhSi(OCH₂CH₂)₂NCH₃ (VII) it is 2.175 Å that is only slightly shorter than in HPhSi(OCH₂CH₂)₂NCH₃ (2.206 Å).

No intermolecular hydrogen bonds were observed in the structure of I. Molecular packing in the crystalline structure is realized

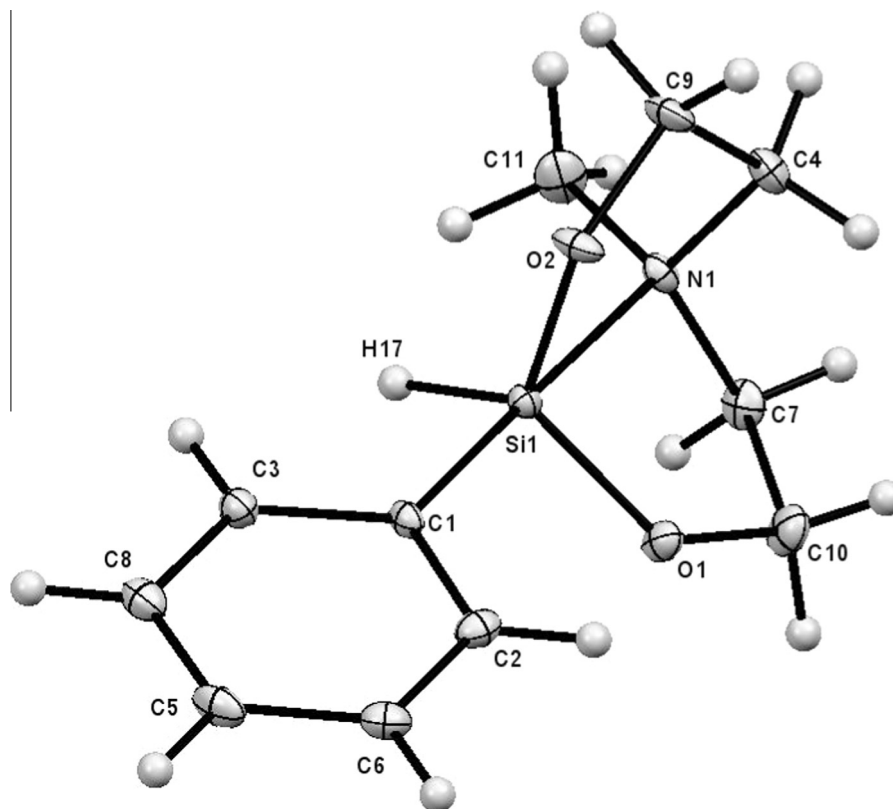


Fig. 1. Molecular structure of **I** with atom numbering.

by Van-der-Waals interactions. These contacts involve both oxygen atoms and phenyl ring hydrogens, while each oxygen atom is linked with phenyl hydrogens of different molecules (Fig. 2). These weak interactions, however influence the geometry of a molecule, making geometry parameters of two five-membered heterocycles SiOCCN unequal and affecting the rotation of the phenyl group. As we will discuss below, quantum chemical methods predict an isolated molecule **I** in the boat–chair conformation to

have a C_s symmetry. Packing Van-der-Waals interactions lead to the distortion of this structure.

The scan of the potential energy surface (PES) by the B3LYP/aug-cc-pVDZ method allowed us to locate four energy minima (Fig. 3). The global one corresponds to the boat–chair configuration of the Si–(OCC)₂–N skeleton. It belongs to the C_s point group and the phenyl ring plane is parallel to the H–Si–N plane. The structure with these planes being orthogonal has almost similar geometry parameters but possesses one imaginary frequency. Thus, it is transition state (barrier) for the rotation around the SiC bond. The height of this barrier is ca. 1 kcal/mol and therefore the rotation is nearly free.

The structure with the boat–boat configuration of skeleton lies 4 kcal/mol higher in energy.

It has no symmetry elements. The phenyl group plane in this conformation is nearly parallel to the H–Si–N plane. It is interesting that the angle by which phenyl group is twisted from the parallel position (H17–Si1–C2–C3 torsion) coincides, maybe fortuitously, with this angle found in the crystal structure. Despite the fact that BB conformation is slightly higher in energy than BC, the Si⋯N interatomic distance is shorter in the former (Fig. 3). This contradicts the opinion that the main factor of the stability of compounds with transannular interactions is the strength of this interaction. The equilibrium B3LYP Si⋯N distance in **I** noticeably exceeds this bond length refined in the crystal structure. This is in line with general trend that the length of the equilibrium Si⋯N distance in silatranes and silocanes obtained by DFT methods reproduces well the experimental Si⋯N bond length in the gas phase, but substantially overestimates interatomic distances defined in X-ray studies of corresponding crystals. The MP2 optimization, probably fortuitously, gives the Si⋯N transannular bond length much closer to the solid state experimental value [21–24]. In our case the same effect is observed. The experimental

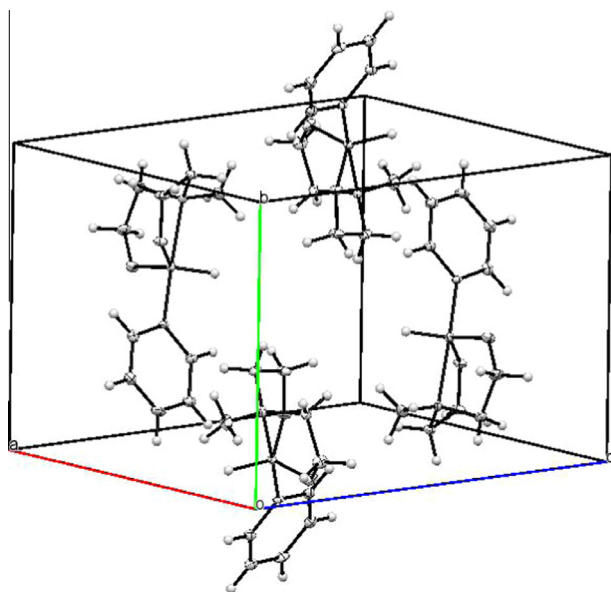


Fig. 2. Packing of phenylhydrosilocene molecules in the crystal unit cell.

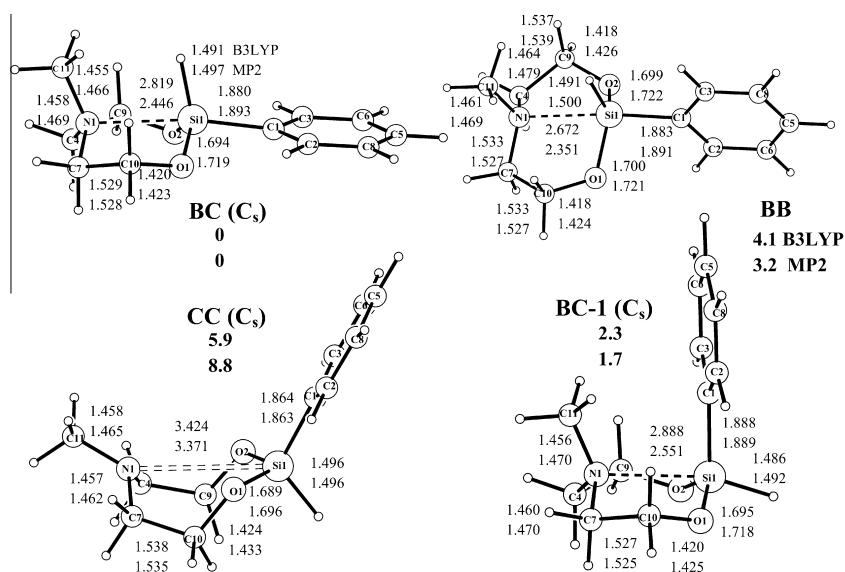


Fig. 3. Equilibrium structures of four conformers of the phenylhydrosilane molecule obtained at the B3LYP and MP2 levels of theory with the aug-cc-pVDZ basis set: boat-chair configuration with axial position of the phenyl group (BC), boat-boat configuration (BB), chair-chair with tetrahedral coordination at Si and without transannular Si...N bonding (CC), and boat-chair configuration with equatorial position of the phenyl group (BC-1). Relative ZPVE corrected equilibrium energies (ΔE_0) in kcal/mol are in bold-face below conformation designations.

X-ray value for the Si...N contact is 2.206 Å. Predicted B3LYP values for the boat-chair conformation (BC) is 2.819 Å and for the boat-boat one (BB) is 2.672 Å (Fig. 3). Note, that despite the higher energy of the BB conformation it has the shorter Si...N distance. MP2 optimized values are much closer to experiment, i.e. 2.446 and 2.351 Å correspondingly. Other optimized bond lengths at the B3LYP and MP2 levels of theory do not differ substantially (Fig. 3).

Dihedral angles which characterize the rotation of the phenyl group (H17–Si1–C1–C3) and the configuration of the Si(OCH₂CH₂)₂N skeleton are summarized in Table 1. The analysis of these data shows that the experimental conformation of the eight-membered heterocycle coincide neither with boat-chair nor with boat-boat configurations of an isolated phenylsilane molecule obtained by quantum chemical methods. This may be exemplified by the analysis of the Si–N–C_α–C_β torsion angles (Table 1). In theoretical models of the BC conformation C_β atoms lie above Si–N–C_α planes, while in the BB conformation they are below (see different signs of corresponding torsion angles in Table 1). In the experimental structure the C_β atom in one five-membered heterocycle is above and in the other below Si–N–C_α planes (Table 1). This kind of the distortion of the structure of an isolated silacyclooctane molecule under crystal packing may be caused by different intermolecular interactions of carbon atoms

in five-membered heterocycles with atoms of neighboring molecules.

The third energy minima corresponds to the chair-chair structure (CC, Fig. 3). As it was proposed earlier [7,8] the transannular Si...N bonding in this conformation is weak or absent. The silicon atom in this form has tetrahedral rather than trigonal bipyramidal coordination. Its energy is only 2 kcal/mol above BC and it may be regarded as an intermediate on the way of interconversion of BC and BC-1. These structures differ in the position of the phenyl ring; in BC-1 it is in the equatorial position. The energy difference of 6 kcal/mol between structures with equatorial (BC-1) and axial (BC) positions of the phenyl group may explain the substituent position exchange in the trigonal bipyramid coordination at Si and freezing of this exchange at lower temperatures observed by Kupce et al. [8].

Conclusions

1. The crystal structure of the title compound C₁₁H₁₇NO₂Si belongs to the space group P21/c, with 4 molecules in the unit cell
2. The Si...N interatomic distance [2.206(3) Å] found in **I** is one of the shortest among determined in ocanes and atranes. It exceeds only the lengths of transannular bond in compounds with highly electronegative fluorine substituents at Si.
3. The phenyl group lies in the axial position and is slightly twisted from the NSiH plane.
4. The B3LYP/aug-cc-pVDZ analysis of the PES has shown that the energy minimum belongs to the boat-chair conformation of C_s symmetry with the axial position of the phenyl group. The lowering of symmetry observed in the X-ray structure may be assigned to Van-der-Waals interactions between ocanes molecules.
5. The predicted structure with the boat-boat configuration of eight-membered heterocycles Si-(OCC)₂-N lies 4 kcal/mol higher than the boat-chair one.
6. Rotation of the phenyl ring around the SiC bond has a barrier less than 1 kcal/mol.

Table 1

Selected experimental dihedral angles and those predicted at the B3LYP and MP2 levels for boat-chair (BC) and boat-boat (BB) conformations of **I** (in degrees).

Dihedral angle	X-ray data	B3LYP		MP2	
		BC	BB	BC	BB
H17–Si1–C1–C3	–21.5(5)	–88.0	–22.4	–87.4	–18.6
N1–Si1–O1–C10	–0.5(3)	–28.9	31.2	–26.2	39.7
N1–Si1–O2–C9	1.1(3)	28.9	–22.2	26.2	–7.2
Si1–N1–C4–C9	–38.0(3)	31.2	–24.8	30.0	–36.4
Si1–N1–C7–C10	–35.3(3)	–31.2	18.4	–30.0	9.2
Si1–O1–C10–C7	–20.8(4)	61.6	–54.4	53.9	–58.0
Si1–O2–C9–C4	–24.9(4)	–61.6	45.6	–53.9	31.5
C11–N1–C7–C10	–158.9(3)	–92.9	–143.3	–89.7	–131.4
C11–N1–C4–C9	84.4(4)	92.9	149.7	89.7	157.3

7. The conformer with the equatorial position of the phenyl group and boat–chair configuration of the skeleton lies 6 kcal/mol higher. The exchange between positions of the phenyl group at silicon proceeds through the chair–chair configuration in which the Si···N transannular bond is absent and coordination at silicon is tetrahedral rather than trigonal–bipyramidal of other conformers.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.molstruc.2015.03.061>.

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